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COMPLETE SPECIFICATION

A process for improving the Stability of Polyolefines

We, VEREINIGTE GLANZSTOFF FABRIKEN A.G. of Wuppertal-Eilberfeld, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for improving the stability of polyolefines.

It is known that polyolefines of high molecular weight and having desirable properties can be produced by the so-called low-pressure polymerisation processes. These products can be further processed, *inter alia* into filaments, films and other shaped elements. However, although the polymers have advantageous properties, such as a high strength and resistance to chemicals, they have a low stability with respect to attack caused by oxidation, more especially towards oxidation in the presence of heat or ultra-violet radiation. The damage which the polymers suffer under such conditions is attributed to the existence of double bonds in or on the chain molecules. From past experience, it does not appear to be possible to avoid the occurrence of double bonds of means of any precautions taken during the polymerisation. Thus, it is necessary to attempt to subject the prepared polymer to an after-treatment, by which a neutralisation of the double bonds is achieved and thus an improvement in the stability of the polyolefines.

A known treatment for this purpose has been carried out with silicon compounds, in which at least one hydrogen atom is directly bonded to the silicon atom. With this known process, the polyolefines must be dissolved in a solvent to form a solution and stirred for a relatively long time with the silicon compound and a suitable catalyst. Apart from that fact that considerable quantities of solvents and precipitants must be used for this purpose, this process is extremely troublesome, because the actual treatment must be followed by a

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precipitation and purification of the polymer. However, according to an alternative proposal the treatment can be carried out in such a way that the polyolefine is mixed with the silicon compound in an extruder at relatively high temperatures of for example 250 to 300°C, but it is not possible to obtain a uniform stabilisation with this method of procedure. In addition, the silicon compound remains in the polymer, and this is disadvantageous.

Another known process attempts to solve the problem by carrying out a hydrogenation of the double bonds. The polyolefine is conducted in solution, emulsion or suspension, together with hydrogen, through a hydrogenation arrangement in which it is brought into contact with a suitable hydrogenation catalyst. The process requires a considerable expenditure for apparatus and time and is not suitable for the treatment of large quantities of polyolefine. This working method also has the disadvantage that the hydrogenation catalyst has to be removed as otherwise, if it remained in the polyolefine, it would lead to disturbances during subsequent processing.

The present invention provides a process for improving the stability of polyolefines, which comprises dispersing purified polyolefine powder in an inert hydrocarbon, admixing therewith 0.1 to 1% by weight (based on the polyolefine) of an organic sulphur compound of the general formula



(wherein R is an alkyl radical containing 1 to 18 carbon atoms, an aralkyl radical, an aryl radical, a cycloalkyl radical, or an alkyl ester radical), heating the mixture while stirring, either in the presence of 0.01 to 0.1% by weight (based on the polyolefine) of an organic peroxide at temperatures from 60°C up to the boiling point of the inert medium for 30 minutes to 5 hours, or under the action of ultra-violet rays at temperatures between

20°C and the boiling point of the inert medium for 30 to 60 minutes, separating the polyolefine and washing it several times with the inert medium.

- 5 We have found that an improvement in the stability can be achieved in a simple manner in accordance with the invention.

Preferred organic sulphur compounds are: aliphatic mercaptans containing 2 to 18 carbon atoms in the molecule, cyclohexylmercaptan, thiophenol, benzyl mercaptan, amyl mercapto acetate and lauryl- β -mercapto propionate. Because of the smaller nuisance due to odour, the difficultly volatile compounds of higher molecular weight are preferred.

- 15 Organic peroxides which can be used include di-*t*-butyl peroxide, dibenzoyl-, dicumyl-, diacetyl-, dilauroyl-, cyclohexanone and methylethylketone peroxides, *t*-butyl peracetate and *t*-butylperbenzoate.

20 Examples of inert media are such inert hydrocarbons as pentane, hexane, heptane, benzene, benzene, toluene, xylene, decalin, tetralin and diesel oil. Preferred inert media are readily volatile compounds, because of the easier regeneration and the more rapid removal from the polymer.

- 30 In certain circumstances it may be expedient to work at temperatures which are higher than the boiling point of the inert medium at normal pressure. In these cases, the pressure should be raised accordingly.

By comparison with the known processes, the present invention offers the advantage that 35 the treatment of the polymers can take place immediately following the purification in the same apparatus as that in which the purification has been carried out. All the inert media which can be used for the process are solvents 40 which can also be used in the purification. Excess of the organic sulphur compound can be removed by suction filtering the polymer, which can be easily purified by washing with the inert medium. A separate purification of 45 the polymer from a heterogeneous catalyst, as is necessary with the known hydrogenation, can be omitted with the process according to the invention. A more uniform and better intensity of the stabilisation is obtained with

the treatment of the polymer powder by the dissolved treating agent than when a stabilising agent is incorporated as granules.

The following Examples illustrate the invention:

EXAMPLE 1 Peroxide catalysis.

Using a 1-litre two-necked spherical flask provided with a stirrer device and reflux condenser and under a nitrogen atmosphere, 100 g. of polypropylene powder (which had been prepared by using aluminium triethyl and TiCl₄ and, after completing polymerisation, purified with hexane and thereafter with methanolic hydrochloric acid solution, and washed neutral and then dried) were dispersed in 600 ml. of an inert medium. A treating agent (i.e. an organic sulphur compound) and also a peroxide were added to the dispersion, which was heated while stirring. The inert medium was separated by suction filtering the powder, which was washed twice, each time with 100 ml. of inert medium, and dried under nitrogen in a vacuum drying chamber. The dry specimen was then ready for determining the stability. The agents used and results obtained are shown in the Table:

EXAMPLE 2

Exposure to ultra-violet light.

Using a 1-litre two-necked spherical flask equipped with a stirrer device and mercury immersion lamp (70 watts) and in a nitrogen atmosphere, 100 g. of polypropylene powder, prepared as described in Example 1, were dispersed in 600 ml. of inert medium. A treating agent was added to the dispersion and then the stirrer device and ultra-violet lamp were switched on. Because of the heat evolved by the lamp, the flask was cooled externally with water. In order to avoid too strong a degradation, the lamp was switched off for 5 minutes each time after being on for 2 minutes. Thereafter, the polymer was filtered off with suction, washed twice with 100 ml. of inert medium and dried, and was then ready for measuring the stability.

The details of the agents used and results obtained are seen from the following Table.

Additive	Quantity in %	Peroxide	%	UV— light	Duration	Temp. °C.	Inert medium	Stability +) min.
Stearyl mercaptan	1	dibenzoyl peroxide	0.1	—	4 h	98	Heptane	92
Amyl mercaptoacetate	1	"	0.1	—	4 h	98	"	100
Amyl mercaptoacetate	1	—	—	+	1 h	20	"	100
Lauryl-β-mercapto-propionate	1	dibenzoyl peroxide	0.1	—	4 h	98	"	82
Lauryl-β-mercapto-propionate	1	—	—	+	1 h	20	"	95
Thiophenol	0.5	Dicumyl peroxide	0.05	—	3 h	60	Hexane	75
Benzylmercaptan	0.75	di-tert-butyl peroxide	0.075	—	4 h	80	Benzene	85
Benzylmercaptan	0.75	—	—	+	1 h	80	"	90
—	—	—	—	+	1 h	20	Heptane	56
—	—	dibenzoyl peroxide	0.1	—	4 h	98	"	47
++ Stearylmercaptan	1	di-tert- butyl peroxide	0.1	—	4 h	98	"	10
+++ Stearylmercaptan	1	—	—	+	1 h	98	"	12
+++ —	—	di-tert- butyl peroxide	0.1	—	4 h	98	"	3

Footnotes to Table.

- 5 +) For determining the stability of the samples, 30 g. of the polymer powder were ground in a ball mill for 30 minutes with a stabiliser mixture of 0.03 g. of dilaurylthiodipropionate and 0.03 g. of 4,4'-thio-bis-(3-methyl-6-*t*-butyl-phenol) (0.1% by weight in each case). 12 g. were pressed at 170°C. in a platen press under a pressure of 350 atm. to form a plate with a thickness of 1 mm. The plate was cut into strips which were 3—4 mm. wide and 30—40 mm. long, of which 3 g. were introduced into a test tube which was in an aluminium block at $200 \pm 1.5^\circ\text{C}$. and was connected to an O_2 burette. By controlling the volume of O_2 , the time in minutes after which spontaneous absorption of O_2 started was established. This induction period for the oxidation of the polymer at 200°C . in pure O_2 served as a standard for the stability at room temperature. In the case of the poly-4-methyl-1-pentene, the measurement was carried out at 230°C . The stabilised, unpressed powder was used.
- 25 ++) These examples relate to poly - 4 - methyl - 1 - pentene.
- 30

WHAT WE CLAIM IS:—

1. A process for improving the stability of polyolefines, which comprises dispersing purified polyolefine powder in an inert hydro-

carbon, admixing therewith 0.1 to 1% by weight (based on the polyolefine) of an organic sulphur compound of the general formula



(wherein R is an alkyl radical containing 1 to 18 carbon atoms, an aralkyl radical, an aryl radical, a cycloalkyl radical or an alkyl ester radical), heating the mixture while stirring, either in the presence of 0.01 to 0.1% by weight (based on the polyolefine) of an organic peroxide at temperatures from 60°C up to the boiling point of the inert medium for 30 minutes to 5 hours, or under the action of ultra-violet rays at temperatures between 20°C and the boiling point of the inert medium for 30 to 60 minutes, separating the polyolefine and washing it several times with the inert medium.

2. A process as claimed in claim 1, wherein the polyolefine is separated by suction filtration.

3. A process as claimed in claim 1 or claim 2, wherein the polyolefine is polypropylene.

4. A process as claimed in claim 1, substantially as described with reference to either of the Examples.

5. Polyolefines when stabilised by the process claimed in any of the preceding claims.

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